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Non - Chromium Conversion Coatings on Aluminium

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Introduction

In the current period our efforts were concentrated on the without chromate passivation of Al 2024-T3. This material is known to be very prone to both pitting and intergranular corrosion owing to high Cu content (its composition- 4.5% Cu, 1.5% Mg, 0.6% Mn) and heat treatment prehistory (solution heat-treated, then strain-hardened). Corrosion accelerates especially in the presence of halogen ions. The actual mechanism by which the Cl^- or F^- ions affect corrosion of Al and its alloys is not fully understood, but has been attributed to the interaction between the ions and the protective oxide layer[1,2]. The following phenomena are responsible for Al 2024 T3 enhanced susceptibility to corrosion.

1. Enhanced cathodic depolarization.
2. Enhanced permeability of Al oxide layer on the material surface.
3. Galvanic corrosion.

Although increased Cu additions were found to lead to more positive open-circuit and oxide-breakdown potential, Cu, whether present as a precipitate or as a dissolved alloy constituent, promotes cathodic depolarization[2-4]. Consequently, the susceptibility of the alloy to corrosion is enhanced. It is not clear whether Cu promotes cracking of the oxide layer or causes an intrinsic loss of electrical resistance of the Al oxide.

During age hardening of the alloys with Cu content more than 2 wt%, particularly Al 2024, intermetallic Θ -phase CuAl_2 precipitates. Formation of the equilibrium Θ -phase (CuAl_2) caused a decrease in the breakdown potential. Since precipitation is much more rapid at grain boundaries than within grains, the nonuniform Cu enrichment of the boundaries gives rise to a Cu-depleted region adjacent to the grain boundaries. This leads to corrosion at or near the

grain boundaries due to the formation of galvanic cells between cathodic Cu-rich areas and the anodic Cu-depleted zones.

Background.

The use of chromium as an anticorrosion pretreatment ingredient to protect aluminium alloys is being restricted because of environmental concerns. In spite of considerable amount of the works directed to searching environmentally compliant substitutes for Cr, only a few of them gave satisfactory results for Al 2024 T3. Sequences of stage for these processes and achieved corrosion resistance are shown in Schemes 1-5. All alternative processes comprise at least two necessary pretreatment stages. They are cleaning-degreasing and deoxidizing. Conditions of these stages and solutions used are defined by passivation method. In some cases the additional pretreatment stages can be applied. After every stage water rinsing is used.

In Scheme 1 the stages of the process reported by Bibber in 1988[7] are shown. Pretreatment procedure in this process comprise mild non-silicate alkaline cleaning additionally to degreasing and deoxidizing. The step of oxide film formation proceeds at high temperature in boiling water or in the steam stream. As a result an oxide film with the thickness of 0.3 - 0.5 μm is formed. Further three sealing steps follow: they are treatment in aluminium salt, proprietary permanganate and silicate solutions. These stages proceed at high temperature. Coatings produced by permanganate passivation fulfill the requirements to corrosion resistance. They passed standard corrosion test.

Modified Ce permanganate process (Scheme 2) [8] also comprises one or two high temperature stages. Specific sequences of treatments are necessary. Variant 1 and 2 provide 268 and 336 h salt spray tests respectively. Variant 3 provides the same corrosion resistance as variant 2 but also the increased adhesion to acrylic paints.

Modified Ce-molybdate process[9] is shown in Scheme 3.

In this process pretreatment procedure comprise anodic polarization in nitrate solution for 30 min. Surface modification consists of three processes, two of them proceed at 100°C in Ce salt solution, and one is anodic polarization in molybdate solution. Every stage lasts 2 hr, so duration of the process more than 6 h. In spite of the considerable effectiveness of this process its application in the industry is problematical. Although treatment according Scheme 3 drastically increases corrosion resistance of Al 2024 T3, the treated samples have not passed ASTM B 117 corrosion test.

Deposition of talc coating (Scheme 4) [10] is the most close to conventional procedure of chromium passivation. It comprises alkaline degreasing, deoxidizing and deposition of conversion coating in alkaline solution of lithium salt. Corrosion resistance of this layer on Al 2024 T3 is unsatisfactory. Talc coated and heat treated samples of Al 1100 passed 168 h salt spray testing while Al 2024 T3 failed.

Passivation in trivalent chromium solution(Scheme 5)[11] comprises deposition of conversion chromium solution layer from trivalent chromium solution and compulsory post treatment in peroxide or permanganate solution. Without post treatment the acceptable level of corrosion resistance could not be reached. Considered processes suffered from the following disadvantages. All of them are multistage processes, characterized by long duration and usage of high temperatures. This conditions are impractical especially for treating assembled aircraft. As it can be seen from above data the best results were obtained using permanganate solutions, which are instable.

It should be noted that none of the processes which provide acceptable results is a simple conversion process. Combination of different treatments allowed to achieve considerable enhancement of corrosion resistance likely owing to synergistic effect of different elements. At the first stage of the present

investigation we studied applicability of the single stage conversion process basing on different combinations of zirconium, cerium, zinc/phosphate, molybdate/phosphate, permanganate and acrylic compounds.

Sceme 1

PERMANGANATE PASSIVATION

J.W. Bibber, 1988

- * Degreasing
- * Mild non- silicated alkaline cleaner
- * Deoxidizer
- * Oxide film formation
Boiling water 5 min or steam (121-149°C) 1 min
⇒ Film 0.3-0.5 μm
- * Sealing step 1
Aluminium salt solution > 95°C
Rinsing in D.I. water
- * Sealing step 2
Proprietary Permanganate solution > 60°C 1 min or longer
Rinsing in D.I. water
- * Sealing Stage 3 (is only used for on unpainted metal parts)
Silicate solution > 95°C 1.0-1.5 min

Corrosion resistance:

5% Neutral Salt Spray (ASTM B-117)

168 hours

336 hours

No surface corrosion

A few small surface spots

Scheme 2

MODIFIED Ce - PERMANGANATE PROCESS

R.N.Miller,1993

Examples of solutions used for treatment

| A | B | C |
|-------------------------|--------------------------------------|--|
| 50 ml H ₂ O | 500 ml H ₂ O | 90 ml C ₂ H ₅ OH |
| 5 g CeCl ₃ | 5 g Na ₂ MoO ₄ | 5 ml Phenyltrimethoxysilane |
| 0.2 g KMnO ₄ | 5 g NaNO ₂ | 5 ml Glycidoxy(epoxy)polyfunctionalmethoxysilane |
| | 3 g Na ₂ SiO ₃ | |

Sequence of treatments

1.
 - * Solution B 93°C 10 min
 - * Solution A 25° C 5 min
2.
 - * Solution B 93°C 10 min
 - * Solution A 25° C 5 min
 - * Solution B 93 °C 10 min
3.
 - * Solution B 93°C 10 min
 - * Solution A 25° C 5 min
 - * swabbing by solution C

Corrosion resistance

ASTM B - 117

| Sequence | Salt spray,h |
|----------|--------------|
| 1 | 268 |
| 2 | 336 |
| 3 | 336 |

Scheme 3

MODIFIED Ce-Mo PROCESS

F.Mansfeld ,J.Wang, 1994

Pretreatment procedure

- * Cleaning and degreasing- immersion in Alconox for 1 min
- * Deoxidizing- immersion in Diversey 560 for 10 min. Solution contains 25% H_2SO_4 , 15% HNO_3 , 2% H_2SiF_6
- * Copper removal - Polarization in 0.5 M NaNO_3 + 0.67 M HNO_3 at - 55 mV (SCE) for 30 min

Surface modification

1. Immersion in 10 mM $\text{Ce}(\text{NO}_3)_3$ at 100°C for 2 hr, than rinsing in distilled water
2. Polarizing in 0.1 M Na_2MoO_4 at + 100 mV (Hg/HgSO_4) for 2 hr, than rinsing in distilled water
3. Immersion in 5 mM CeCl_3 at 100°C for 2 hr, then rinsing in distilled water

Corrosion resistance

Immersion in 0.5 M NaCl

| As received material | Copper removal only | All process stages |
|--|--------------------------------|-------------------------------------|
| Pits spread over the surface within 3 days | 8 % area affected after 7 days | 0.065 % area affected after 30 days |

Scheme 4

DEPOSITION OF TALC COATING

R.G.Buchheit, M.D. Bode, G.E. Stoner, 1994

Processing stages for talc coatings

- | | | | |
|---|---------------------|---------|--------|
| * | Alkaline degreasing | 65°C | 5 min |
| * | Acid deoxidizing | Ambient | 5 min |
| * | Talc coating | Ambient | 15 min |

Solution composition $\text{Li}_2\text{CO}_3 + \text{LiOH}$ Coating composition $\text{Li}_2[\text{Al}_2(\text{OH})_6]_2 \text{CO}_3 \cdot n\text{H}_2\text{O}$

- * Aging at temperatures 25 - 300 ° C

Corrosion resistance

ASTM B 117 - 90

Talc- coated and heat treated samples of Al 1100 passed 168 h salt spray testing, while Al 2024-3T failed.

Scheme 5

PASSIVATION IN TRIVALENT CHROMIUM SOLUTIONS

F.Pearlstein, V .S. Agarwala,1995

Deposition of conversion layer

- * Immersion in proprietary alkaline cleaner 55°C 30 min
- * Immersion in proprietary non chromate deoxidizer 25°C, 15 min
- * Immersion in passivating solution 25°C 5-40 min

Solution composition: 4 g/l $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$ [from commercial preparation -
 26 % Cr_2O_3 and 23 % Na_2SO_4], 0.4 g/l Na_2SiF_6 , 20 ml/l 0.5 N
 NaOH ; pH 3.7.

Post treatment
 (one of the following)

1. None
2. 30 sec in 10 - ml/l H_2O_2 (30%) in deionized water at 25 °C and drain-dried without rinsing
3. 30 sec in 5 g/l KMnO_4 at 25 °C ; water - rinsed and drain -dried

*Corrosion ratings of panels treated in trivalent chromium**bath after 333 hr salt spray exposure at different**post treatment*

1.
 Considerable
 about 25 %
 area affected

2.
 Moderate
 about 5%
 area affected

3.
 No corrosion

Experimental

Sample preparation was as follows. As received samples were first degreased using detergent of composition shown in Table 1. Temperature and time were 50 °C and 10 min respectively. After that samples were rinsed in distilled water to remove the detergent. The second stage was deoxidizing treatment in the 20 % H_3PO_4 . Finally, the samples were rinsed with distilled water to remove the deoxidizing solution. Passivation procedures were carried out for 1-10 min. at temperature not higher than 70°C.

The effectiveness of the passivation procedures was estimated by two corrosion tests: potentiodynamic measurements and salt spray test. Instruments Princeton Applied Research Model 283 potentiostat was used for potentiodynamic measurements. Experiments were run at scan rate 2mV/sec in 5% NaCl solution. Salt spray tests were conducted according ASTM B 117 in salt spray cabinet NOA, ISO 9002. Samples were checked in every two hours and test was continued till appearance of a few small corrosion spots on the surface of the sample. Structure of the deposited layers was examined using SEM model ISM 840 JEOL, Japan and Optical Microscope Olympus BN. Coating composition was determined by EDS and Auger analysis.

Results and discussion

I. Deposition of conversion coatings.

The best results were obtained for molybdate/phosphate conversion process. However, they are also unsatisfactory as can be seen from Table. 2 Introduction of the acrylic latex additive in the conversion solution improved corrosion resistance to some extent, while acrylic latex top coating increased corrosion resistance noticeably. The comparison of data for Al 1100 shows dramatic inferiority of the conversion layers on Al 2024 3T.

Thus our results confirm the impossibility to produce effective protective coating on Al 2024 by means of conversion process. Explanation for this situation seems to be as follows. All conversion processes proceed with active participation of the alloy surface. Surface nonuniformity of the material causes nonuniformity of produced conversion layers. It, in its turn, contributes to galvanic corrosion.

Thus, to achieve the desirable level of protection, the layers of another non conversion nature have to be used.

II. Deposition under external polarization

We studied deposition of protective layers from zinc phosphate solutions under external cathodic polarization. Usual equipment for plating was used. Deposition was carried out with zinc anodes. The effects of solution composition, temperature and current density were studied.

1. Effect of zinc salt used for solution preparation.

Some compositions based on zinc phosphate and zinc nitrate are shown in Table 3. No positive result was obtained. Solutions with pH 4.5-6.0 were turbid and did not provide deposition of layers. Layers deposited from transparent solutions with pH 3.3 and 10 did not exhibit protective effect.

On the other hand, solutions prepared on the base of zinc carbonate enabled to produce excellent protective layers. These solutions comprise zinc carbonate, phosphoric and nitric acids.

2. Effect of phosphoric acid concentration in zinc carbonate solutions.

Effect of H_3PO_3 content was studied for the solution containing 6 g/L ZnCO_3 and 4 ml/L HNO_3 . In this case at least 8 ml/L of H_3PO_4 is necessary to produce transparent solution and achieve good corrosion resistance. The further increase of phosphoric acid resulted in drastic decrease of corrosion resistance (Table 4). Along with this, the layer structure changed from star like to

fine crystalline. When concentration of H_3PO_4 increased to 16 ml/L, no coating was formed.

3. Effect of ZnCO_3 concentration.

To investigate effect of ZnCO_3 concentration solutions containing 12 g/L ZnCO_3 and 3 g/L ZnCO_3 were prepared. $\text{ZnCO}_3 : \text{H}_3\text{PO}_4$ ratio for them was the same as for composition shown in Table 4. As can be seen from the data in Table 5 the layers deposited from concentrated solution passed 312 hour salt spray test, while those from diluted solution passed only 48 hour test.

4. Effect of nitric acid.

The effect of nitric acid was investigated for solution with 6 g/L ZnCO_3 and shown in Table 6. At its contents lower than 2 ml/L it is impossible to obtain transparent solution. At 2 ml/L fine crystalline coatings were formed. They passed 24 hour corrosion test. In the range 3-4 ml/L star like crystalline coatings with high corrosion resistance were produced. The further increase of nitric acid content led to the sharp decrease of stars concentration on the sample surface and reduction of corrosion resistance.

Obtained data show that only coatings with specific star like crystalline structure exhibited high corrosion resistance. The formation process of star like crystalline layers is shown in Fig 1. At the initial stages the separate stars grow on the surface. At the following stages, these separate stars occupy more area and finally interfere to give continuous coating. Microscopic observation allows to reveal coarse star like crystals with size of about 200 μm . Coatings with thickness of 5-7 μm were formed for 6 min. Flat adjacent stars superimpose. This superposition contributes, likely, to isolation of material surface from corrosive environment.

5. Effect of cerium containing additives.

According literature data[12] cerium inhibits corrosion of Al 2024 alloy by reducing the rate of the cathodic reaction. This was due to the formation of

cerium-rich films over copper containing intermetallics which act as local cathodic sites. Results from tests carried out on an aluminium/copper galvanic couple, which was used to simulate the electrochemical behaviour of the copper containing intermetallics, showed that corrosion inhibition was associated with the formation of a Ce-rich film over the copper in agreement with that observed for the alloy.

To introduce Ce in the protective layer, we attempted incorporation of Ce - containing additives in zinc phosphate solution. Their compositions are shown in Table 7. Corrosion stains appeared after 1-5 hour corrosion test. Thus no positive effect of Ce incorporation was observed. In opposite Ce additives destroyed the specific structure of layers and drastically reduced corrosion resistance.

6. Effect of the electrolyte temperature was investigated in the temperature range 30-70°C. At low temperature(30°C) no coating was formed, while at high temperature (70°C) fine crystalline coating with low corrosion resistance was produced. The temperature range 40-60°C allowed to deposit the coatings consisted of coarse star like crystals (Table 8). These coatings passed more than 300 hour corrosion test. View of two samples after 380 hour test is shown in Fig. 2. It should be noted that some samples stood the corrosion attack for time up to 500 hours.

7. Effect of current density is shown in Fig 3. Noticeable deposition on the surface began only at 0.25 A/dm² but layers produced at this current density passed not more than 5 hour; at 0.5 A/dm² - about 25 hour. In the range 1-2 A/dm² high corrosion resistance was achieved. Deposition at 2 and 4 A/dm² allowed to lower deposition time to 3 and 1 min respectively without any reduction of corrosion resistance, while the coatings produced at 2 A/dm² for 1 min corroded only after 20 hour salt spray test. Although the enhanced current densities (2-4 A/dm²) provided high corrosion resistance at the reduced

deposition times, the optimum level of current density is 1-1.5 A/dm². Coating deposited at these current density are more uniform, while increasing the current density to 2-4 A/dm² coarse thick unsound coatings appeared on the edges of the samples. Deposition rate at the current equal 1 A/dm² density was measured by weighing method. Results are shown in Table 9. Average deposition rate value was calculated to be about 0.065 g/dm² min.

Deposition potential versus deposition time at constant current density equal to 1 A/dm² is shown in Fig 4. Cathodic potential sharply increased for about 10 sec. after polarization of electrode and then remained at constant level about 1060 - 1080 mV. Potential permanence testifies about sufficient conductivity of deposited layer. It is important for an industrial implementation as a deposition can be carried out at low and constant voltage.

8. Potentiodynamic polarization plots.

Potentiodynamic polarization plots in 5% sodium chloride solutions obtained for as-deposited protective layers and after 30 min conditioning are depicted in Fig. 5. For comparison potentiodynamic polarization plot for Cr passive layer is shown. Polarization plot for as-deposited layer exhibits the range of passivation from about -800mV to -500mV. Corrosion potential is about -900mV, that is considerably lower than in the case of chromium layer. After conditioning this passivation range disappears but corrosion potential shifts considerably in the more positive range and become very close to corrosion potential of chromium layer.

Changes of the potentiodynamic polarization plot reflects first of all the changes of open circuit potential during conditioning. Potential of the protective coating in dependence on the immersion time in 5% NaCl is shown in Fig. 6. When as-deposited layer is immersed in solution its potential is about - 1000mV, however it shifts to considerably more positive values with immersion time and reaches constant level about - 600mV. It is interesting to note that immersion in

distilled water provides the same changes. This fact along with the changes of the potentiodynamic polarization plot forces to suggest that protective action of deposited layers is associated with their hydration and formation of sealed structure which isolates Al 2024 T3 surface from corrosive medium.

9. Composition of protective coating.

Results of EDS analysis are shown in Fig. 7. Coarse star like crystalline coating (OB2) consists mainly of Zn and P. Al content was determined to be <1%. Atomic ratio Zn/P for coating was 1.07, while for $\text{Zn}_3(\text{PO}_4)_2$, ZnHPO_4 and $\text{Zn}(\text{H}_2\text{PO}_4)_2$ - 1.5, 1 and 0.5, respectively. That is the composition of protective coating close to ZnHPO_4 . Auger analysis showed that distribution of the elements inside the deposit is sufficiently uniform (Fig.8b,c). It did not change with sputtering time at least in the depth of 500 - 4000 Å. By ESCA analysis no Zn in metallic form was revealed. Basing on the obtained results the following points can be concluded.

According to Auger analysis the penetration of sodium chloride in the protective layer during corrosion test is impeded. Auger spectra for the sample before (b) and after 240 hour corrosion test (c) were identical (Fig.8b,c). No peaks related to sodium or chloride were revealed.

Summary

1. Simple conversion layers as well as combination of different conversion layers were shown to be ineffective for corrosion protection of Al 2024 T3.
2. New approach the deposition from Zn/phosphate solution under external cathodic polarization was proposed.
3. Effects of composition, temperature and current density on corrosion resistance were investigated. Optimum composition and conditions were defined as follows:

| | |
|----------------------------------|---------------------|
| H_3PO_4 - 8 ml/L | 40-60°C |
| HNO_3 - 4 ml/L | 1 A/dm ² |
| ZnCO_3 - 6 g/L | 5-7 min. |

4. New process has the following advantages:

- * simple
- * non-expensive, uses available materials
- * proceeds at relatively low temperatures
- * short duration

5. Samples of Al 2024 T3 with new protective layer passed more than 300 hour salt spray test.

Program for further investigations.

- * Studying the effect of Al 2024 T3 sample size and form, as well as electrode arrangement in the bath on deposition process.
- * Development of the protective coating on Al 7075 T73.
- * Studying the effect of different pre- and post treatment procedures on corrosion resistance of Al 2024 T3.
- * Investigation of the influence of different post treatment procedures on adhesion to paints used in aircraft industry.

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Table 1
Sample pretreatment

| | | | |
|---------------|---------------------------|-------|----------------------------|
| Degreasing : | Sodium metasilicate | 3 % | 10 min. 50°C |
| | NaH_2PO_4 | 1.2 % | |
| | Na_3PO_4 | 2.5 % | |
| | Soap | 2 % | |
| Deoxidizing : | H_3PO_4 | 30 % | 3 min. ambient temperature |

Table 2

Effect of molybdate/phosphate conversion process on corrosion resistance of aluminium materials.

| Passivation treatment | Time of the salt spray, time till the appearance of corrosion stains, hours | |
|--|---|---------|
| | Al 2024 | Al 1100 |
| Without treatment | 2 | 6 |
| Mo/phosphate treatment | 6 | 43 |
| Mo/phosphate with acrylic latex additive 1ml/L | 27 | 70 |
| Mo/phosphate treatment with the acrylic latex post treatment | 72 | 192 |

Composition of solution: Na_2MoO_4 - 12g/L
 H_3PO_4 - 10ml/L
 NaNO_3 - 20g/L

Conditions of conversion process: $T = 40^\circ\text{C}$, $t = 5\text{min}$.

Post treatment by immersion in acrylic latex SERAFON N 7171 and N 7172, mixture 1:1, concentration 1 - 2,5 ml/L

Table 3
Deposition from solutions based on
 $\text{Zn}_3(\text{PO}_4)_2$ and $\text{Zn}(\text{NO}_3)_2$

| N | Composition of solution, g/L | pH | Transparency of solution | Corrosion test in salt spray cabinet ,h |
|---|--|-----|-----------------------------|--|
| 1 | $\text{Zn}_3(\text{PO}_4)_2$ 2 H_3PO_4 1 KHF_2 3 | 3.3 | Transparent | 3 |
| 2 | $\text{Zn}_3(\text{PO}_4)_2$ 5 H_3PO_4 1 KHF_2 3 | 4.5 | Turbid solution | no coating |
| 3 | $\text{Zn}_3(\text{PO}_4)_2$ 5 $\text{Na}_4\text{P}_2\text{O}_7$ 3 $\text{Zn}(\text{NO}_3)_2$ 7 NaNO_3 0.5 | 6,0 | Turbid solution | no coating |
| 4 | $\text{Zn}(\text{NO}_3)_2$ 3 $\text{Na}_4\text{P}_2\text{O}_7$ 12 Na_2MoO_4 12 H_3PO_4 10 | 5.5 | Turbid yellow solution | no coating |
| 5 | $\text{Zn}(\text{NO}_3)_2$ 3 $\text{Na}_4\text{P}_2\text{O}_7$ 12 H_3PO_4 10 | 5.0 | Turbid solution | no coating |
| 6 | $\text{Zn}(\text{NO}_3)_2$ 3 $\text{Na}_4\text{P}_2\text{O}_7$ 12 | 10 | Transparent | 2 |

Conditions of process: $T=40^\circ\text{C}$, $i=0.25\text{A/dm}^2$, $t=5\text{min.}$, etching in 30% H_3PO_4

Table 4

**Effect of H_3PO_4 on quality and corrosion resistance
of phosphating coating on Al 2024 T3.**

| No. | Amount of H_3PO_4 , ml/L | pH | Corrosion test, h | Note |
|-----|--|-----|-------------------|-------------------------------|
| 1 | <8 | | - | No dissolution of carbonate |
| 2 | 8 | 2.2 | 300 | Star like crystalline coating |
| 3 | 10 | 1.8 | 5 | Fine crystalline coating |
| 4 | 12 | 1.7 | 5 | |
| 5 | 16 | 1.5 | 5 | Almost no coating |

$T = 60^\circ\text{C}$, $i = 1 \text{ A/dm}^2$, $t = 7 \text{ min}$, etching 30% H_3PO_4

Composition of solution: ZnCO_3 - 6g/L;

HNO_3 - 4ml/L

Table 5

Effect of ZnCO_3 concentration.

| Solution composition | | | Corrosion test, h | Coating structure |
|-----------------------|--------------------------------|-----------------------|-------------------|-----------------------|
| ZnCO_3 , g/L | H_3PO_4 , ml/L | HNO_3 , ml/L | | |
| 12 | 16 | 4 | 312 | Star like crystalline |
| 3 | 4 | 4 | 48 | Fine crystalline |

$T = 50^\circ\text{C}$, $i = 1 \text{ A/dm}^2$, $t = 5 \text{ min}$.

Table 6

**Effect of HNO_3 on the quality and corrosion
resistance of phosphating coating on Al 2024 T3.**

| No. | Amount of HNO_3 , $d=1.41\text{g/cm}^3, \text{ml/L}$ | pH | Corrosion test, h | Note |
|-----|---|-----|----------------------|---|
| 1 | - | 2.4 | - | No Zn carbonate dissolution. Turbid solution. No coating |
| 2 | 1 | 2.2 | | |
| 3 | 2 | 2.1 | 24 | Fine crystalline coating |
| 4 | 3 | 2.0 | 300-333 | Star like crystalline coating |
| 5 | 4 | 1.9 | | |
| 6 | 5 | 1.9 | 5-20 | Low concentration of stars |
| 7 | 7 | 1.8 | 20 | |
| 8 | 8 | 1.7 | - | No coating |

$T = 60^\circ\text{C}$, $i = 1\text{A/dm}^2$, $t = 7\text{ min}$, etching 30% H_3PO_4 .

Composition of solution: ZnCO_3 - 6g/L

H_3PO_4 - 8ml/L, $d = 1.8\text{g/cm}^3$

Table 7

Composition of Ce-containing additive

| N | Additive, g/L |
|---|---|
| 1 | Ce(NO ₃) ₃ 1 |
| 2 | Ce(NO ₃) ₃ 1 KHF ₂ 3 |
| 3 | Ce(NO ₃) ₃ 1 K ₂ C ₂ O ₄ 3 |
| 4 | Ce(NO ₃) ₃ 1 NH ₄ NO ₃ 5 |
| 5 | Ce(NO ₃) ₃ 1 EDTA 2 |
| 6 | Ce(HSO ₄) ₄ 1 NH ₄ NO ₃ 1 HNO ₃ 2 |

Composition of solution : H_3PO_4 - 8ml/L, Conditions: $T=60^\circ\text{C}$, $i=1\text{A/dm}^2$,
 HNO_3 - 4 ml/L, $t=5\text{min}$.
 ZnCO_3 - 6g/L,

Table 8
Effect of temperature

| Temperature °C | Coating quality | Corrosion test,h |
|----------------|---------------------------|------------------|
| 30 | No coating | - |
| 40 | Star - like | 312 |
| 50 | crystalline | 312 |
| 60 | coating | 312 |
| 70 | Fine crystalline coatings | 100 |

Conditions: 1A/dm^2 , $t=6\text{ min.}$

Table 9

Deposition rate of Zinc phosphate coating

| N | Deposition time, min | Weight increase, g/dm^2 | Weight increase, $\text{g/dm}^2\cdot\text{min}$ |
|---|----------------------|----------------------------------|---|
| 1 | 5 | 0.31 | 0.062 |
| 2 | 7 | 0.40 | 0.057 |
| 3 | 10 | 0.74 | 0.074 |

Composition
of solution :

H_3PO_4 - 8ml/L
 HNO_3 - 4 ml/L
 ZnCO_3 - 6g/L

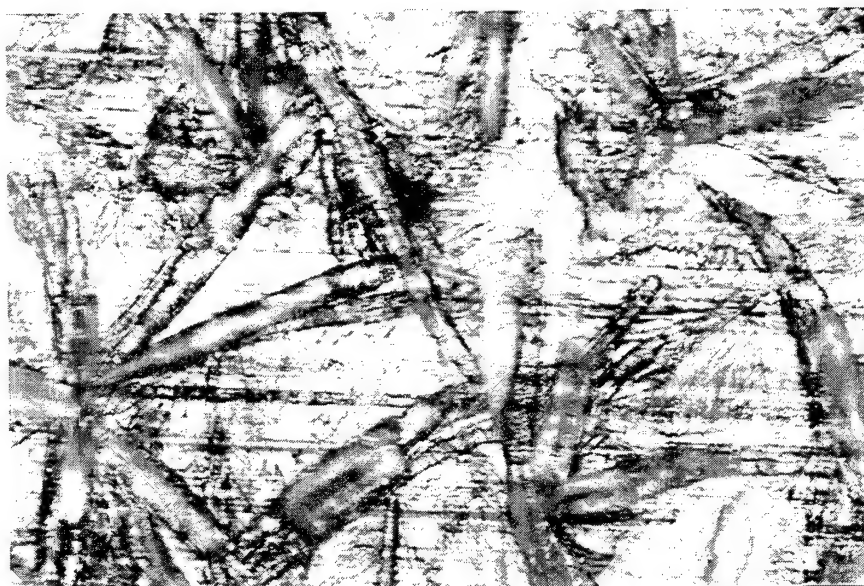
Conditions:

$t=5\text{min.}$
 $i=1\text{A/dm}^2$
 $T=60^\circ\text{C}$

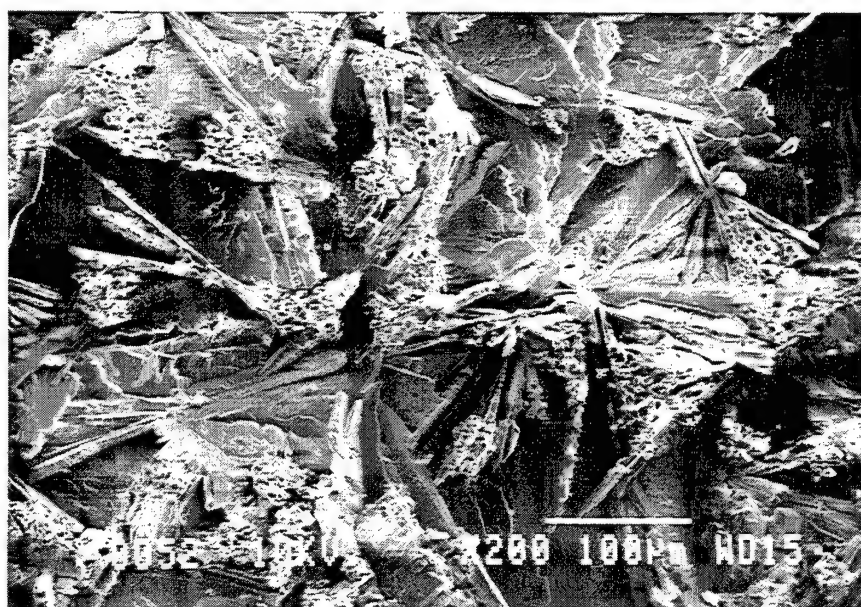
Structure of star like crystalline Zn/phosphate layers



1 min.



3 min.



6 min.

FIG 1

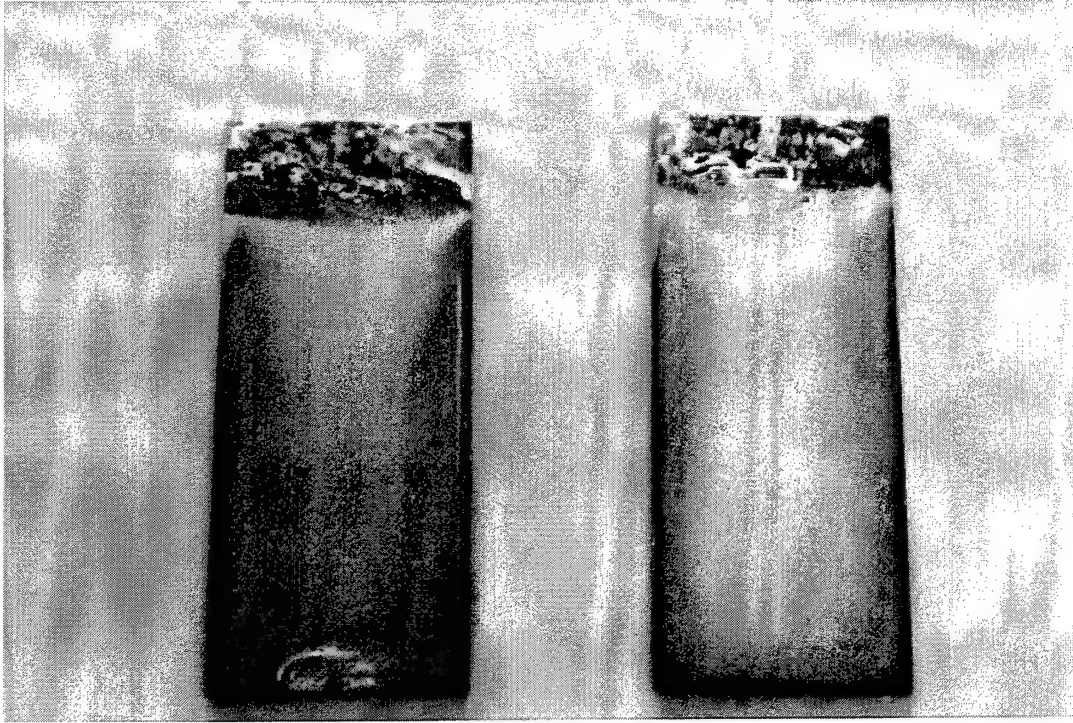


Fig.2 The view of the samples after 380 h corrosion test.

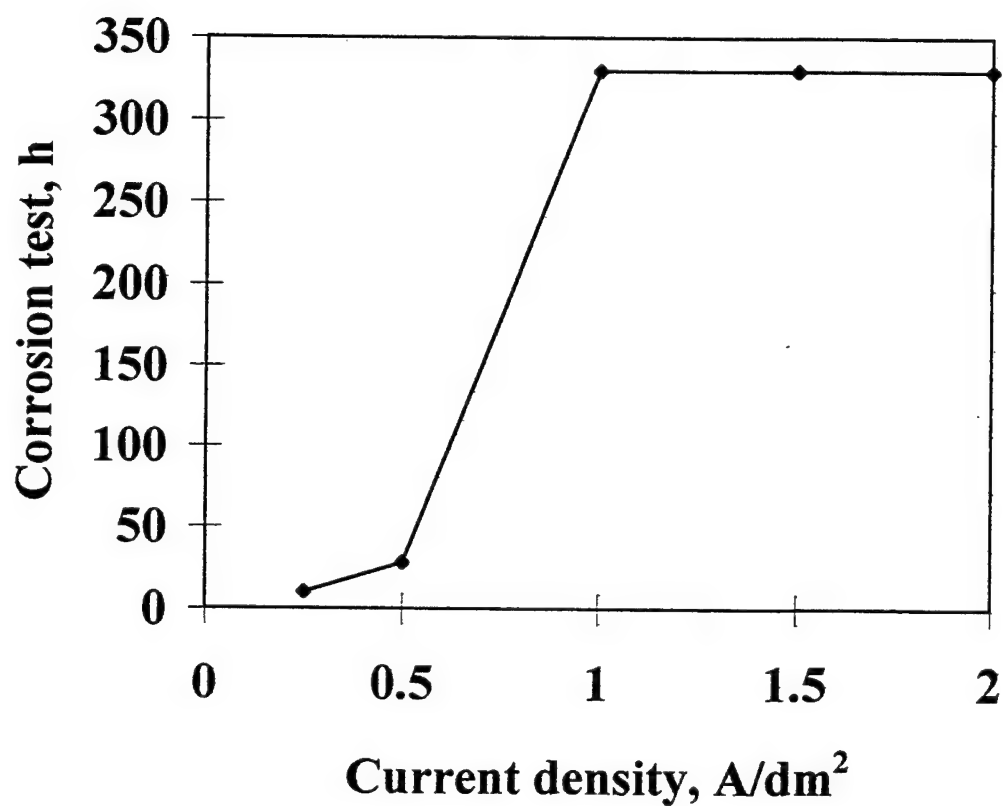


Fig 3 Corrosion resistance versus cathodic current density.

Composition of solution: ZnCO_3 - 6g/L

Conditions $T = 60^\circ\text{C}$

HNO_3 - 4 ml/L

$t = 6 \text{ min.}$

H_3PO_4 - 8 ml/L

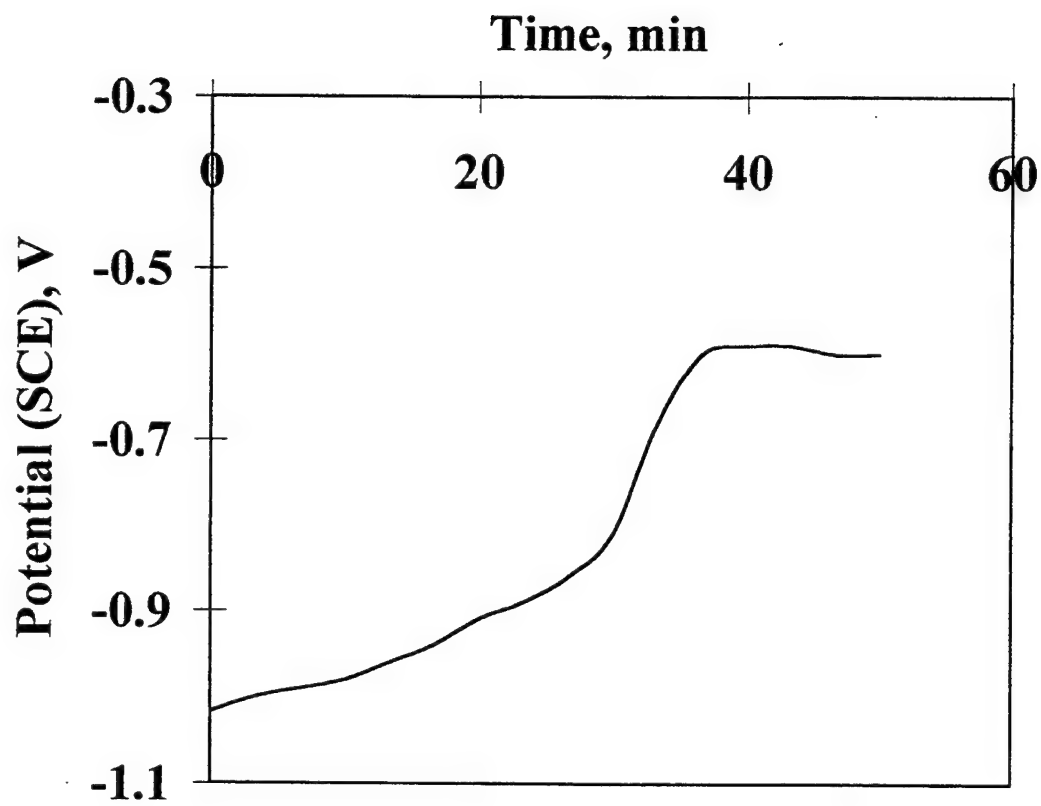
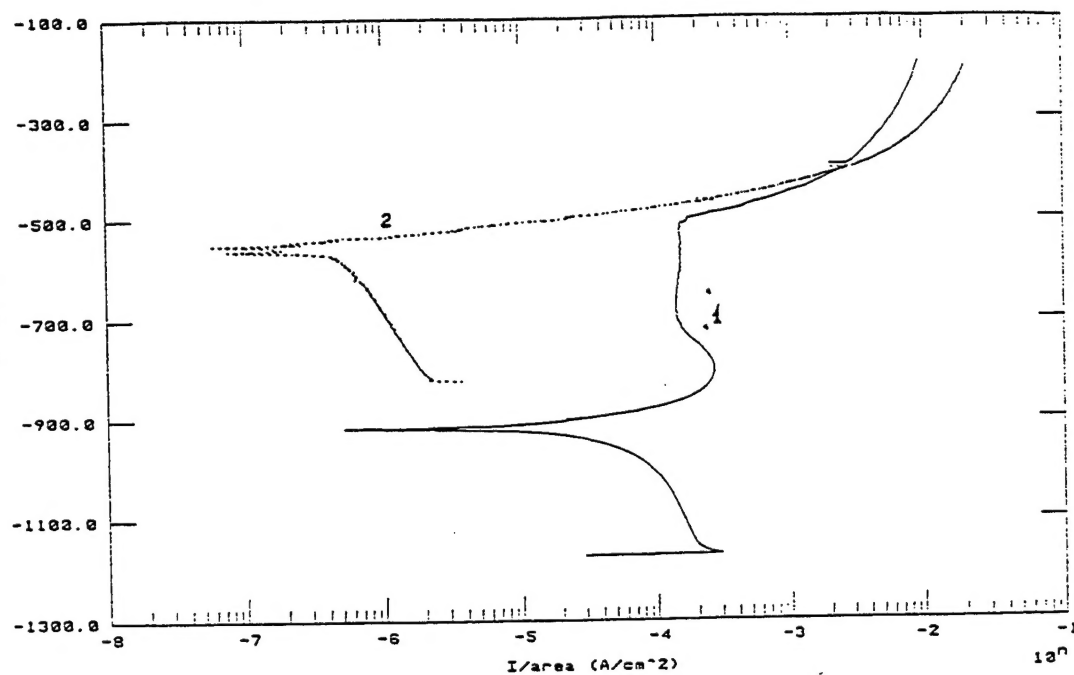
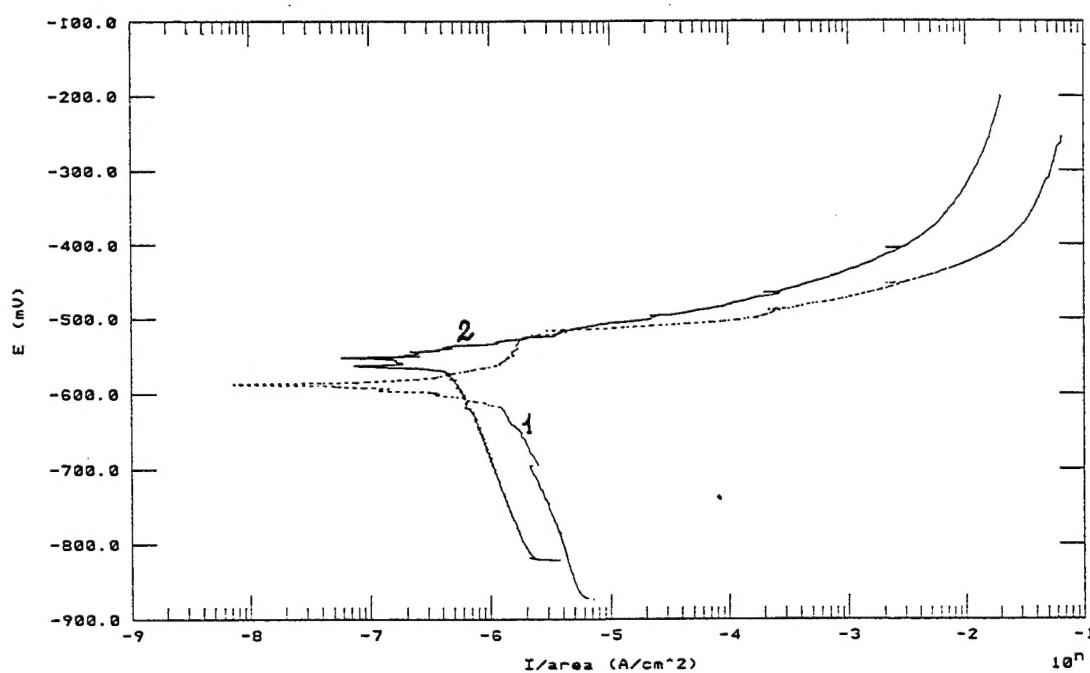


Fig. 4 Deposition potential versus deposition time.

Current density 1 A/dm^2 , 60°C .



a



b

Fig. 5 Potentiodynamic polarization plots in 5% NaCl for samples Al 2024, passivated in chromate passivation solution (2) and in Zn/phosphate solution (1) as deposited (a) and after delay 30 min. in solution (b).

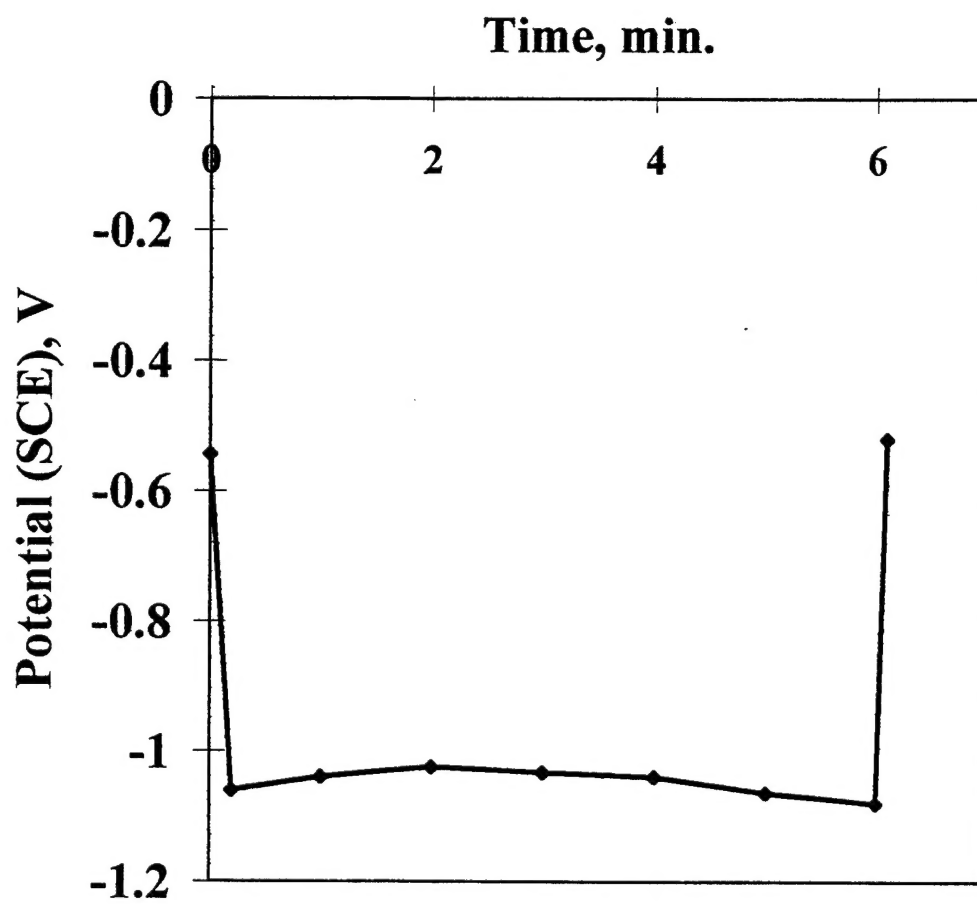


Fig. 6 Potential of Zn - phosphate coating versus time in 5% NaCl.

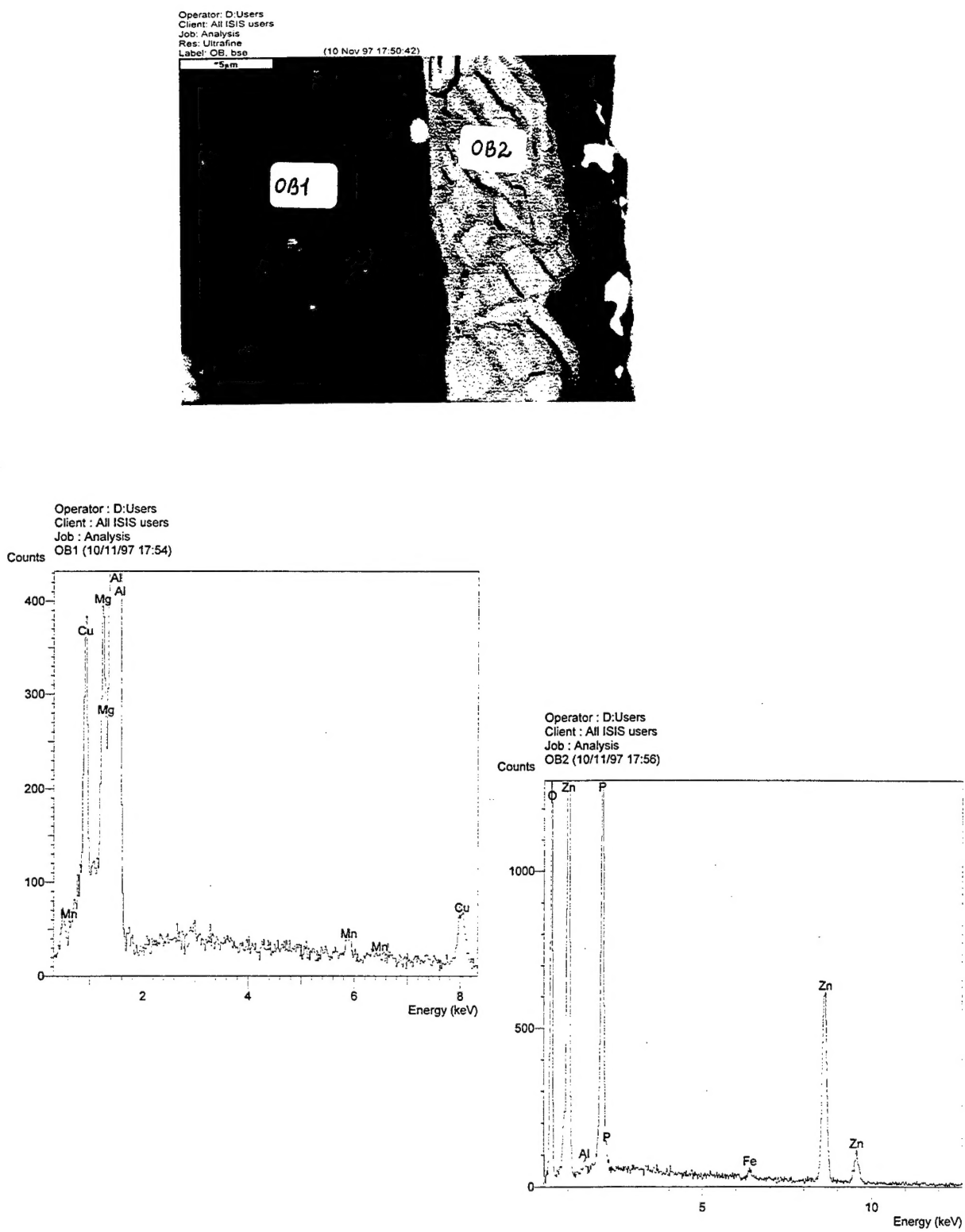


Fig. 7 Results of EDS analysis.

- a - micrograph of the coating;
- b - EDS spectrum of the Al 2024 substrate;
- c - EDS spectrum of the deposited protective layer.

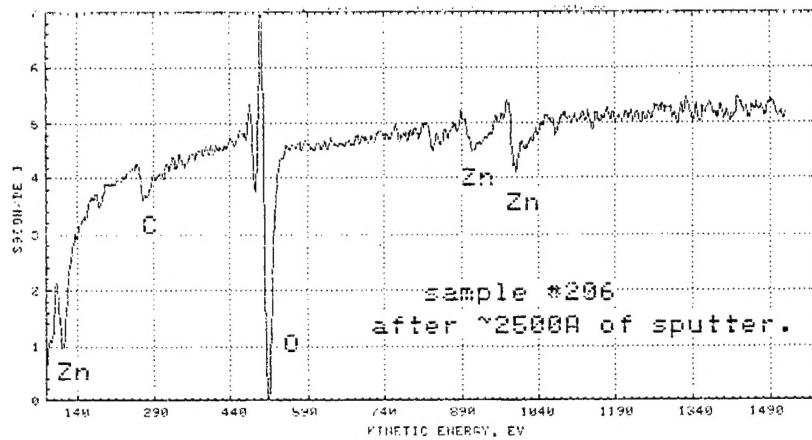
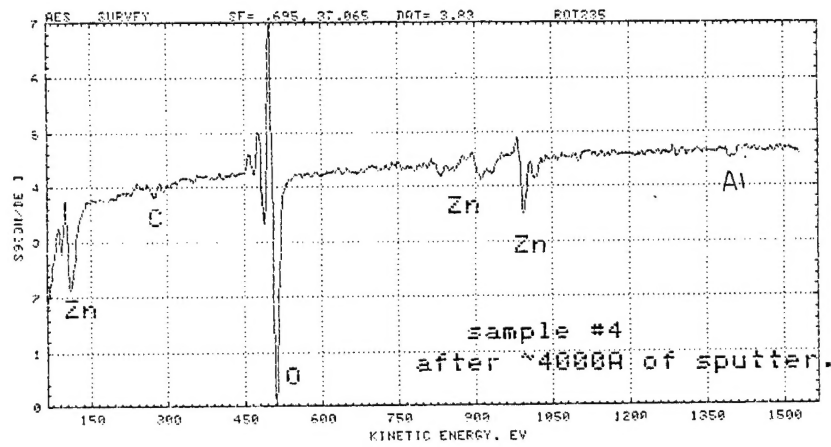
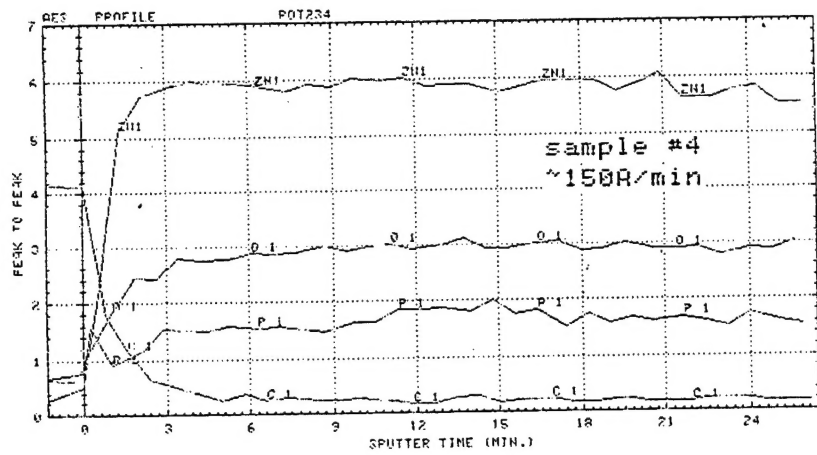


Fig. 8 Results of Auger analysis. Auger profiles (a). Auger spectra for the protective coating before (b) and after 240 hour corrosion test (c).